How heteroatom (N,B,P) doping of CNFs tunes the selectivity in the partial oxidation of propane

Yanila Marco, Laura Roldán, Edgar Muñoz, Enrique García-Bordejé

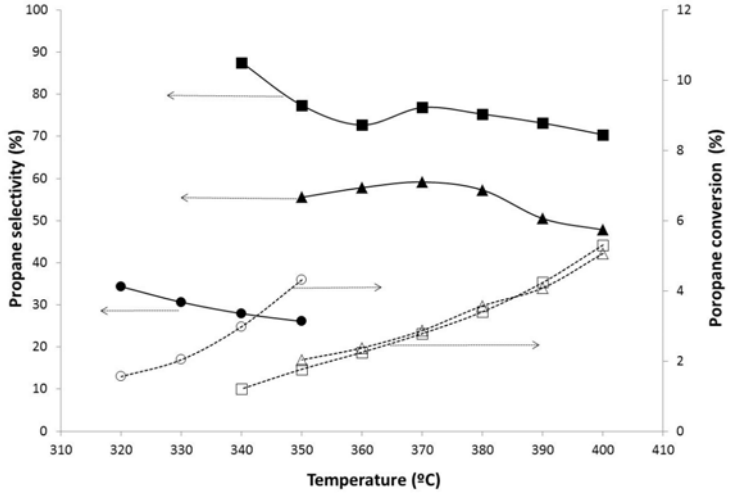
Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza, Spain, jegarcia@icb.csic.es

CNT and other carbon nanostructures have been proposed as metal free catalyst for the enhanced oxidative dehydrogenation of alkanes to alkenes. The doping of CNT with B or P resulted in an increase of the selectivity to the corresponding alkene [1]. Here we have used home-prepared CNFs doped with B, P and N for the oxidative dehydrogenation of propane.

Un-doped CNF were grown by CVD of ethane:H_2 (50:50) using 20%Ni/Al_2O_3 catalyst at 600 ºC. The CNF were purified first with NaOH at 80ºC during 4 hours and later with HNO_3 at 100 ºC during 4 hours. As-purified CNF were *ex-situ* doped with B using boric acid or with P using either triphenylphosphine or ammonium phosphate. N-doped CNF were grown by CVD of ethylenediamine using either 20%Ni/Al_2O_3 or 20%Fe/Al_2O_3 and subsequently purified using first NaOH at 80ºC and later with HCl at 100 ºC.

Doped CNF were characterized by XPS, TEM and tested in the oxidative dehydrogenation of propane (15% propane, 15% O_2, N_2 to balance) at low temperatures (<400 ºC).

The doping with more than 2wt% of B or P decreased significantly the conversion compare to pristine CNF. The more remarkable effect on selectivity was found when doping with P using triphenylphosphine. As seen in figure 1, there is an increase of 20 points in selectivity for P-CNF with respect to pristine CNF for the same conversion. N-doped CNF are more active than the other CNFs because the activation of O_2 is enhanced but the selectivity is steered to total oxidation to CO_2. In addition, N-CNF are less stable to oxidation than the other CNFs. For this reason, N-CNF are not suitable for this reaction in gas phase but are a promising catalyst for oxidation reactions in liquid phase at low temperatures such as ORR.



Propane conversion (empty symbols) and propene selectivity (filled symbols) as function of the temperature for several catalysts: CNF(△,▲), P-doped CNF prepared from PPh_3 (□, ■), N-doped CNF (○,●). Different feed flow rates were used to obtain similar values of conversion.

[1] B. Frank, J. Zhang J, R. Blume, R. Schlögl, D. Su, Angewandte Chemie International Edition 48(2009), 6913-7.